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Final Report for Period: 07/1997 - 06/2003

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Principal Investigator: Yiacoumi, Sotira .

Award ID: 9702356

Organization: GA Tech Res Corp - GIT

Title:

CAREER: Influence of Soption Rates on Particle Flocculation Kinetics

Project Participants

Senior Personnel

Name: Yiacoumi, Sotira

Worked for more than 160 Hours: Yes

Contribution to Project:

Post-doc

Graduate Student

Name: Chin, C.J. Monica

Worked for more than 160 Hours: Yes

Contribution to Project:

C.J. Monica Chin graduated with a Ph.D. in Environmental Engineering in 2001. Her dissertation topic was 'Aggregation of Colloidal Particles and Breakup of Aggregates: Probing Interparticle Forces,' and was supported by this project. She is now an Assistant Professor in the Graduate Institute of Environmental Engineering, National Central University, Tao-yuan, Taiwan.

Name: Subramaniam, Kavitha

Worked for more than 160 Hours: Yes

Contribution to Project:

Kavitha Subramaniam graduated with a Ph.D. in Environmental Engineering in 2000. Her dissertation topic was 'Metal Uptake and Its Effects on Colloidal Particle Interactions: Equilibria and Rates,' and was supported by this project. She is now a Project Environmental Engineer at Environ Corporation, Princeton, NJ.

Name: Ying, T.-Y. Tony

Worked for more than 160 Hours: Yes

Contribution to Project:

T.-Y. Tony Ying graduated with a Ph.D. in Environmental Engineering in 2001. His dissertation topic was 'Novel Environmental Processes Using Electric and Magnetic Fields,' and was partially supported by this project. He is now a Postdoctoral Research Scientist at the Los Alamos National Laboratory, Los Alamos, NM.

Name: Yang, Kun-Lin

Worked for more than 160 Hours: Yes

Contribution to Project:

Kun-Lin Yang graduated with a Ph.D. in Environmental Engineering in 2002. His dissertation topic was 'Electrical Double-Layer Formation at the Nanoscale: Molecular Modeling and Applications,' and was partially supported by this project. He is now a Postdoctoral Research Scientist in the Department of Chemical Engineering at the University of Wisconsin-Madison, WI.

Name: Shin, Won-Tae

Worked for more than 160 Hours: Yes

Contribution to Project:

Won-Tae Shin graduated with a Ph.D. in Environmental Engineering in 2000. His dissertation topic was 'Effects of Electric Fields on Fluids: Applications in Ozonation,' and was partially supported by this project. He is now a Research Program Manager at the Korea Science and Engineering Foundation (KOSEFO), Taejon, South Korea.

Name: Sung, Youlboong

Worked for more than 160 Hours: Yes

Contribution to Project:

Youlboong Sung graduated with an M.S. in Environmental Engineering in 1999. His research topic was 'Precipitation Effects in Sorption of Metal Ions from Aqueous Solutions,' and was partially supported by this project. He is now a doctoral student in the Environmental Engineering Program at the Georgia Institute of Technology (GIT).

Name: Benesch, Thorben

Worked for more than 160 Hours: Yes

Contribution to Project:

Thorben Benesch graduated with an M.S. degree in 2002. His research topic was 'Like-Charge Attraction of Colloidal Particles in Confined Space,' and was partially supported by this project. He is now an Engineer at BASF, Ludwigshafen, Germany.

Name: Vithayaveroj, Viriya

Worked for more than 160 Hours: Yes

Contribution to Project:

Viriya Vithayaveroj is a Ph.D. student in Environmental Engineering. Her dissertation topic is 'Atomic Force Miscroscopy for Sorption Studies,' and has been partially supported by this project.

Name: Chen, J. Paul

Worked for more than 160 Hours: Yes

Contribution to Project:

J. Paul Chen graduated with a Ph.D. in Environmental Engineering in 1997. His dissertation topic was 'Sorption of Metal Ions from Aqueous Solutions: Equilibrium, Kinetics, and Transport,' and was partially supported by this project. He is now an Assistant Professor in the Department of Chemical and Environmental Engineering at the National University of Singapore.

Undergraduate Student

Name: Tobin, Cara

Worked for more than 160 Hours: Yes

Contribution to Project:

Cara C. Tobin graduated with a B.S. in Civil Engineering in 1999. Her research topic was 'A Unified Approach for Sorption and Particle Flocculation Kinetics,' and was supported by this project. She was awarded an NSF graduate fellowship in 1999 and in the same year she began graduate studies in the Department of Civil and Environmental Engineering at Stanford University.

Technician, Programmer

Other Participant

Research Experience for Undergraduates

Organizational Partners

Oak Ridge National Laboratory

We collaborated with Oak Ridge National Laboratory (ORNL) researchers in examining the influence of electromagnetic fields on environmental processes. Furthermore, we extended our collaboration with Dr. Costas Tsouris, a research staff member at ORNL, in using specialized equipment needed for the project and in modeling phenomena between interacting particles.

Digital Instruments Inc

Digital Instruments (DI) is a private company that manufactures atomic force microscopy (AFM) equipment systems. An AFM system was acquired from DI with partial funding from this project and was used for direct measurements of colloidal interparticle forces during sorption. The company is very much interested in the application of its AFM system in the environmental engineering area, and granted us an equipment donation.

Electric Power Research Institute

Electric Power Research Institute (EPRI), which is a non-profit private organization, has supported a grant on 'Experiments and Modeling of Electrohydrodynamic Ozonation.' The EPRI grant fccused on the use of electric forces to enhance environmental remediation technologies

Lynntech, Inc.

Lynntech, which is a private research company, has supported research on 'Soil-Ozone Interactions: Kinetics and Mathematical Simulation.' This research focused on the use of ozone in environmental remediation technologies. This topic is a direct extension of this project in which basic mechanisms are investigated in environmental particulate systems.

Other Collaborators or Contacts

We collaborated with Dr. Eric Guibal and his group at L' Ecole de Mines d'Alès in France to model biosorption of metal ions from aqueous solutions.

We collaborated with Dr. Stanley Grant and Dr. Scarlet Relle at the University of California-Irvine to study secondary minimum aggregation of colloidal particles.

We collaborated with Dr. J. Paul Chen (assistant professor at the National University of Singapore), who was supported through this project during the final stages of his doctoral research at the Georgia Institute of Technology (GIT), to model sorption of metal ions by engineered particles and transport of metal ions in subsurface systems.

We collaborated with Dr. E. Steven Vittoratos, a senior scientist at Chevron Research and Technology Company, in the characterization of the surface area and porosity of some porous materials used in this project.

Activities and Findings

Research and Education Activities:

This program was comprised of fundamental studies focused on the behavior of colloidal particles in aqueous suspensions during sorption of ions. Experimental, theoretical, and computational methods were employed to investigate the behavior of fine particles in chemically varying aquatic environments with the main objective to better understand the fate of ionic species and colloidal particles in natural and engineered aquatic systems. The results may be used in a number of engineered processes that have as objectives the removal of particles and ions from aqueous suspensions, treatment of wastewaters prior to discharge in the environment, or the deliberate separation of manufactured particles. Extensions of this research were also investigated with major objective to better understand sorption and colloidal phenomena in environmental systems, and to quantify the influence of electromagnetic fields on environmental processes.

The educational plan of this program involved the development of courses that emphasize mathematical modeling of environmental systems, incorporation of research results into courses, and student participation in experimental work at a National Laboratory.

Details on the specific research and educational activities are given below.

Research activities

Experimental efforts covered a wide range of activities with sorption and colloidal particle aggregation as the central themes. A number of experimental methods were employed including Atomic Force Microscopy (AFM), a capability acquired in the Principal Investigator's (PI) laboratory for surface imaging and colloidal force measurements, Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) for simultaneous visualization and identification of chemical species, cyclic voltammetry for electrical characterization of conductive surfaces, light scattering for particle size measurements, electrophoretic mobility for zeta potential measurements, laser Doppler velocimetry for particle velocity measurements, electric and magnetic fields inducing external forces, and other analytical methods for concentration measurements. In addition, bench-scale apparatuses have been set up for sorption and aggregation studies including equilibrium and kinetics.

In one part of the work (carried out by Dr. K. Subramaniam, Ph.D. 2000), two metal ion sorbates (cadmium and copper) and two metal oxide sorbents (ferric oxide and silicon dioxide) were used in sorption and particle-interaction experiments. Detailed characterization studies such as determination of surface charge, specific surface area, pore-size distribution, initial particle size distribution, and density were carried out for both sorbents. Equilibrium uptake of sorbates was studied as a function of pH at different ionic strengths. Changes in the particle zeta potential, suspension pH, metal ion concentration, and particle size distribution were monitored in sorption equilibrium experiments. The experiments successfully reproduced expected trends of concentration, zeta potential, and pH variations, and their validity was verified in a number of independent experiments. Kinetic experiments were then conducted to study the dynamics of sorption and particle interactions in shear flow regimes during metal ion uptake. Changes in the size distribution of the sorbent particles were measured at different times during the kinetic experiments to quantify particle aggregation during metal ion uptake. Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) measurements were carried out in order to compare the differences in the extent of binding of copper onto different sites on the oxide particles (Mr. Y. Sung, M.S. 1999). Precipitation of copper appeared to occur along with uptake in our equilibrium experiments in high pH ranges. To further understand this observation, copper precipitation was studied as a function of pH using copper nitrate solutions. X-Ray Diffraction (XRD) measurements were carried out to identify the precipitate as tenorite (CuO).

A methodology was developed to measure surface forces during sorption of copper ions using Atomic Force Microscopy (AFM) (Dr. C.J. Chin, Ph.D. 2001; Ms. V. Vithayaveroj, Ph.D. 2004). Surface forces between a single colloidal particle of a metal oxide sorbent and a plate were directly measured with and without sorption of copper ions. Direct force measurements showed that the force is repulsive and its magnitude decreases with increasing ionic strength and decreasing pH. The surface force was calculated based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, including van der Waals and electrostatic forces, for constant surface charge and compared with AFM data. The DLVO theory agreed well with force measurements and was, thus, used to represent the forces during the sorption of copper ions. In intermediate-pH solutions, sorption of copper ions caused charge reversal for the silica particle from negative to positive and, therefore, the force between the silica particle and the glass plate changed from repulsive to attractive. The transient zeta potential of the silica particle during the sorption of copper ions was determined by representing the experimental data with the DLVO theory.

In parallel to AFM measurements, an external magnetic field was employed to quantify interparticle forces. In this case, the external force required to cause transition from secondary- to primary-minimum aggregation of superparamagnetic colloidal latex particles was investigated. An external magnetic force and a suspension of colloidal superparamagnetic particles comprised the model system. The external magnetic force was used as an additional force to manipulate the total interparticle force. The magnetic induction needed for this transition was calculated from the extended DLVO theory, which included van der Waals, electrostatic, and magnetic-dipole forces, as well as non-DLVO hydrophobic attraction and steric repulsion. The magnetic induction at which the transition from secondary-minimum to primary-minimum aggregation occurs was experimentally determined from visualization of chain formation and breakup. Experimental and theoretical transitional magnetic inductions showed good agreement for small particles in a narrow capillary tube and large particles in a wide capillary tube. The agreement observed for small particles in both 50-micrometer and 100-micrometer capillary tubes and large particles in 100-micrometer capillary tubes showed that the DLVO theory and the existing formulae for interparticle potential calculations are reliable. Effects of surfactant molecules on the transition from secondary- to primary-minimum aggregation were also investigated. Observations showed that the transitional magnetic induction increases with increasing surfactant concentration until the particles are completely covered by surfactant molecules. The advantage of this method is that it is non-invasive and provides a particle-particle force rather than a particle-plate force. The disadvantage is that it requires the use of magnetic particles of known magnetic susceptibility.

The use of external forces, such as electric and magnetic forces, in water and wastewater treatment was investigated with the objective to improve existing processes including particle aggregation, filtration, and sorption (Dr. T.-Y. Ying, Ph.D. 2001). Magnetically induced aggregation of particles was investigated both theoretically and experimentally in terms of particle-particle forces, colloidal stability, and aggregation kinetics. High-gradient magnetic filtration (HGMF) based on filters packed with a ferromagnetic wire was analyzed in terms of particle-collector forces. The collector was a ferromagnetic wire of cylindrical shape. A magnetic seeding technique was developed with the objective to cause aggregation of magnetic particles with nonmagnetic particles and aggregates and produce aggregates of positive magnetic susceptibility. These aggregates were then removed by HGMF. The magnetic particles used were magnetite-containing particles. An electrocoagulation method was also developed to co-precipitate metal ions and form magnetic particles in situ by means of electric current. The major advantages of this method are (i) efficient removal of dissolved contaminants and (ii) formation of magnetic particles, which incorporate the contaminants and can be easily removed by magnetic filtration. Experiments with various types of water contaminated with copper ions were conducted. The efficiency of the process in removing copper ions was evaluated by measuring the concentration in the solution before and after the treatment. The formed particles were characterized by X-ray diffraction analysis and scanning electron microscopy.

Electrosorption was employed with carbon-based materials, such as carbon aerogel, to remove ions from aqueous solutions (Dr. T.-Y. Ying, Ph.D. 2001; Dr. K.-L. Yang, Ph.D. 2002). A low-voltage potential was applied to a pair of high-surface-area electrodes facing each other and ions accumulated in the double layer near the interface. The capacity of the electrodes with respect to applied potential was experimentally obtained. Cyclic voltammetry experiments were conducted at various solution concentrations and scanning rates to study the electrical double layer formation in nanostructured carbon aerogel. Results showed that carbon aerogel is a good electrical double layer capacitor (EDLC), which can be divided into mesoporous and microporous capacitors. The mesoporous capacitor showed fast charging/discharging response that is barely affected by the concentration and scanning rate. Therefore, the specific capacitance of mesoporous capacitors is constant over a wide range of electrical potential. On the other hand, the microporous capacitor showed slow charging/discharging response and its capacitance strongly depended on solution concentration and potential. Unlike other experiments in which only a flat minimum is observed at the point of zero charge (pzc), a deep minimum was observed near the pzc at low solution concentrations when a slow scan rate was used. This unique feature is a result of electrical double layer (EDL) overlapping in the micropores, which is consistent with predictions by the Stern model. Based on this behavior, a new approach was suggested for pzc measurements of solid porous materials having a great portion of their surface area in the micropore region.

In addition to solid particles, microbubbles were also investigated in terms of formation, interface transport, and reaction with organic species in the solution (Dr. W.-T. Shin, Ph.D. 2000). In this part of the work, a novel concept for interphase mass-transfer enhancement using electrostatic spraying was investigated. This method generates large amounts of surface area of one fluid dispersed into another, therefore, it has the potential to be more efficient than traditionally used techniques. Electrostatic spraying was applied to enhance ozonation of organic compounds in water. Oxygen was introduced in an ozone generator and the effluent stream consisting mainly of oxygen and ozone was introduced into an aqueous solution through an electrified metal capillary. Due to the potential between the capillary and the grounded water, the gas stream formed microbubbles into the water. The mass-transfer enhancement of ozone from the gas phase to the aqueous solution, due to the high surface area generated by electrostatic spraying, was investigated and compared to the conventional method of bubble diffuser. The oxidation efficiency of phenol by electrostatic ozonation was examined as a function of gas flow-rate, electrostatic potential, and ozone concentration. In the case that oxygen is introduced directly through the capillary under corona discharge, electrons interact with oxygen molecules to form radical, highly reactive species that may carry oxidation reactions in the solution. The formation of microbubbles in a number of solvents was also investigated.

A surface complexation model was developed to describe the surface charge of the amphoteric sorbent particles as a function of pH. Changes in the zeta potential and the extent of sorption of metal ions by oxide particles were estimated. This model has been linked with particle interaction models to provide the collision efficiencies and size distribution changes of sorbent particles under different solution conditions, such as pH and ionic strength. A mathematical approach, based on trajectory analysis, was developed to describe particle interactions in shear-flow systems. The findings showed that the aggregation rate is enhanced by increasing the shear rate. In addition, computer simulations were carried out to directly observe the secondary minimum separations between two interacting particles. It was found that an increase in attractive forces could decrease the secondary minimum separations. Modeling work was also conducted to describe sorption of metal ions by engineered particles, transport of metal ions in subsurface systems, and sorption of natural organic matter by iron hydrous oxides. The effect of hydrodynamic resistance was also examined in a model developed to predict the performance of a two-step magnetically seeded filtration process that included heterogeneous flocculation (shear-flow and Brownian) and magnetic filtration.

The formation of EDL was simulated by grand canonical Monte Carlo (GCMC) and canonical Monte Carlo (CMC) methods (Dr. K.-L. Yang, Ph.D. 2002). In the GCMC simulation, a primitive EDL model was used, in which water was considered as a continuum and the ions were considered as hard spheres. Results were slightly different from those predicted by the Poisson-Boltzmann equations at moderate values of concentration and applied voltage. These results were used as an initial condition for the CMC study for a non-primitive model, where the EDL was composed of molecular water, cations, and anions. The non-primitive model, in which water was not considered as a continuum, provided a very different view of the EDL at the atomistic level. A single layer of water molecules, instead of counterions, was strongly adsorbed on the charged surface. This feature could not be observed when the primitive model was used. Because of this behavior, the maximum counterion concentration occurs at the center of nanopores instead of the surface. This prediction contradicts the classical EDL theory, but is supported by experimental data found in the literature.

One of the prominent open questions in colloidal science is the like charge attraction of colloidal particles in confined geometries or close to charged walls. It has been observed that the pair potential reaches a minimum for a certain sphere-plate distance. A theoretical explanation of this phenomenon has been attempted by consideration of electrostatic interaction as well as hydrodynamic coupling between the spheres and the plate. We reviewed electrostatic and hydrodynamic models available in the literature and compared modeling results with experimental data. The effects of geometrical changes, such as sphere-wall and sphere-sphere separation, as well as the variations in physicochemical parameters, such as the ionic strength and zeta-potential, were analyzed. We showed that the hydrodynamic coupling is the dominating effect, while the electrostatic influence may be often neglected. Some observations, however, could only be explained by means of a combined electrostatic-hydrodynamic model that was derived in this program (Mr. T. Benesch, M.S. 2002). While the hydrodynamic model predicts a monotonically decreasing pair potential for decreasing sphere plate distance, a potential minimum can be computed with the combined model for a certain sphere-to-wall distance as found in the literature.

The influence of a wall on the Brownian motion of a sphere was also theoretically investigated. Even though the developed model could be extended for highly symmetric arrangements of two walls, no analytical solutions were available for the problem of a second boundary. Through recent advances in image processing, semiempirical formulas could be extracted from experiments, which showed that the walls and the hydrodynamic coupling of colloidal spheres effect an attractive pair potential. Equations that describe confined Brownian motion are useful to compute the migrating of particles in porous media or near fluid-solid boundaries, the diffusion of macromolecules in membranes, as well as the interaction of cells with surfaces. In this work an earlier approach based on the single-wall reflection method was extended. This modified version provided predictions for the perpendicular and parallel diffusion coefficients that matched better with experimental data reported in the literature than other available models including the linear superposition approximation (LSA), coherent superposition approximation (CSA), and Oseen's equation.

Education activities

Three courses were offered, Process Principles in Environmental Engineering, Modeling of Sorption Processes, and Separation Processes, to graduate students in Environmental Engineering at GIT, and one course, Environmental Engineering Systems, to undergraduate students in the School of Civil and Environmental Engineering at GIT. All four courses emphasize mathematical modeling of environmental systems. In the Modeling of Sorption Processes and Separation Processes, which cover sorption phenomena to a great extent, results from the research part of this program were incorporated into the lectures and discussed with students. In addition, all three graduate courses were offered through the Distance Learning Program of GIT and, therefore, reached industrial researchers and practitioners.

This project, in association with additional funding from the School of Civil and Environmental Engineering at GIT, supported the education of ten students. An undergraduate student, C.C. Tobin, who was introduced to the project with the objective to motivate her to pursue doctoral studies in environmental engineering, went on to graduate school at Stanford University. She gave a presentation of the research she has conducted and discussed her research experiences in front of the undergraduate students who took Environmental Engineering Systems. Y. Sung and T. Benesch were partially supported and graduated with M.S. degrees in Environmental Engineering in 1999 and 2002, respectively. Seven Ph.D. students (J.P. Chen, W.-T. Shin, K. Subramaniam, C.J. Chin, T.-Y. Ying, K.-L. Yang, and V. Vithayaveroj) were fully or partially supported through this project conducting related research for their dissertations. They all presented the findings of their doctoral research in seminar sessions offered as part of the Modeling of Sorption Processes and Separation Processes courses. Shin, Chin, Subramaniam, and Ying were visiting students for periods of approximately six months at the Oak Ridge National Laboratory (ORNL), using state-of-the-art equipment and experimental techniques needed in their research. Chin also spent a few days in December 1998, at the facilities of Digital Instruments (DI) in Santa Barbara, CA, working with the company scientists on using AFM in measuring colloidal interparticle forces.

Findings:

The research activities in this project were focused on fundamental questions and hypotheses related to interfacial forces and phenomena occurring between surfaces in aqueous solutions. Some of the results had immediate application in the development of novel processes for water and wastewater treatment. Other results were more basic and helped us understand better the behavior of both natural and engineered environmental systems. The major findings resulting from this project are listed as follows.

1. Predictive models describing sorption of metal ions from aqueous solutions and aggregation of colloidal particles in various flow regimes have been developed and verified by experimental data. Sorption of metal ions was modeled through surface complexation reactions, which included the pH effect. Aggregation of fine particles was based on particle collision frequencies and sticking efficiencies which both are functions of the flow regime. Brownian diffusion, turbulent shear, and gravity sedimentation mechanisms were considered, as well as the influence of external forces, such as electric and magnetic forces.

2. A novel magnetic seeding method was introduced for particle aggregation and magnetic filtration. This method was proven in the laboratory and modeled as a two-step process. A bivariate population balance model was developed for the aggregation of particles and a high-gradient magnetic filtration model was developed for particle filtration. The magnetic-seeding technique was developed for the removal of fine particulates from aqueous suspensions that could not be efficiently removed by other means. A small commercial company named Sulmet, LLC has built a commercial magnetic separation unit based on this concept that is currently used in wastewater treatment.

3. A novel electrocoagulation method has been developed for co-precipitation and in-situ magnetic seeding of colloidal particles in suspensions. When employed for pure solutions of sodium chloride, this method produced magnetite particles of high purity. The electrocoagulation method together with high-gradient magnetic filtration has been demonstrated as an effective approach to separate metal ions from aqueous solutions.

4. A novel electrosorption method has been investigated for the removal of ions from aqueous solutions. Ions are accumulated in the electrical double layer at the solid-liquid interface of electrically activated electrodes of high surface area. This method has implications in water treatment as well as in supercapacitors for energy storage and aqueous cleaning processes.

5. It was found that there is a limit of pore size below which pores do not contribute to electrosorption due to the electrical double-layer overlapping effect. The significance of this finding is in the synthesis of materials for electrosorption. Specifically, there is an optimum pore size associated with the ionic strength of the solution and the applied potential. At this optimum pore size, all pores contribute to electrosorption and the available surface area is at a maximum, which is a desired property. As we decrease the pore size, we make materials of higher specific surface area, but only a fraction is available for electrosorption.

6. Cyclic voltammetry of nanostructured platinum-based materials for electrosorption has shown a size exclusion effect for ions. This means that by synthesizing pores of a specific size, we may have selective electrosorption.

7. A novel electrostatic method has been developed for the formation of microbubbles, containing ozone and radicals, to enhance the transport rates of oxidative species through the gas-liquid interface. The method showed improved oxidation rates of phenol in water and may have applications in water treatment, as well as in the production of ultrapure water. Based on this method, the Electrohydrodynamic Micromixing

Reactor (EMR) was developed at Oak Ridge National Laboratory in collaboration with David DePaoli, Costas Tsouris, and Michael Hu.

8. Methodologies were developed and tested for the direct measurement of surface forces, which are on the order of 1 nN. Two techniques have been developed, the first based on AFM and the second based on the transition from secondary- to primary-minimum aggregation by means of an externally applied magnetic field. Experimental data from both methods compared favorably with the DLVO theory. It was also found that, under strong magnetic fields, the transition from secondary- to primary-minimum aggregation occurs even in suspensions that have been stabilized with surfactant molecules. This finding is relevant to ferrofluids stability and robustness.

9. Monte Carlo techniques have been developed to investigate the electrical double layer in confined geometries. Results showed that a layer of water molecules strongly adsorbs on the charged surface. As the width of a pore becomes smaller, the maximum ion concentration appears in the middle of the pore, which contradicts the Poisson-Boltzmann equation. The reason for this discrepancy is that the Monte Carlo method allows accounting for the effects of water molecules, while the Poisson-Boltzmann equation does not. In this regard, the Monte Carlo method is more accurate. A greater understanding of the electrical double layer formation at the molecular level is very important to many interfacial phenomena occurring in physical, chemical, and biological systems.

10. As expected, Brownian diffusion in confined geometry is retarded. A model has been extended and results compared favorably with experimental data. Applications may be found in transport through membranes and natural systems.

11. Two models, the electrostatic and hydrodynamic models, recently reported in the literature to describe interparticle forces in confined geometry, have been combined to provide more accurate predictions. Applications may be found in transport through membranes and natural systems.

Training and Development:

Several graduate and undergraduate students have worked on this project. A number of them collaborated with researchers in other institutions including companies (Digital Instruments, Chevron, Lynntech), research laboratories (Oak Ridge National Laboratory, Electric Power Research Institute), and universities (Ecole de Mines d'AlÞs in France, National University of Singapore). These interactions involved active participation and visits at the collaborator's site, often for extended periods of time. The experience was proven very beneficial to the students as shown by the career paths they have chosen, as well as their success after graduation.

One undergraduate student (C.C. Tobin), who was introduced to the project with the objective to motivate her to pursue doctoral studies in environmental engineering, has received a fellowship from NSF in 1999 and went on to attend graduate school at Stanford University. One M.S. student (Y. Sung) is currently working on his Ph.D. thesis in Environmental Engineering at GIT, and a second (T. Benesch) is working for BASF. Two Ph.D students (J.P. Chen, C.J. Chin) are now professors of Environmental Engineering and two others (T.-Y. Ying, K.-L. Yang) are currently Postdoctoral Researchers (Los Alamos National Laboratory, University of Wisconsin). The fifth Ph.D. (W.-T. Shin) is at a research institute in Korea, and the sixth (K. Subramaniam) is with Environ. The last one (V. Vithayaveroj) is still working on her Ph.D. thesis in Environmental Engineering.

Most of the students did both experimental and modeling work. Some had the opportunity to work more on experiments, others invested more in modeling, but they all tried to support their results with additional experimental and modeling work. All students had the opportunity to use modern experimental methods including Atomic Force Microscopy (AFM), a capability acquired in the PI's laboratory for surface imaging and colloidal force measurements, Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) for simultaneous visualization and identification of chemical species, cyclic voltammetry for electrical characterization of conductive surfaces, light scattering for particle size measurements, electrophoretic mobility for zeta potential measurements, laser Doppler velocimetry for particle velocity measurements, electric and magnetic fields inducing external forces, and other analytical methods for concentration measurements. In addition, the students had the chance to build bench-scale apparatuses for sorption and aggregation studies including equilibrium and kinetics.

Four of the graduate students, K. Subramaniam, C.J. Chin, T.-Y. Ying and W.-T. Shin, have spent time at ORNL as visiting students, which gave them the opportunity to enhance their research capabilities. In addition, this project gave the PI the chance to visit and work at Oak Ridge National Laboratory for two summers. She has also visited the National University of Singapore for a summer as a visiting professor, where she co-taught a course to undergraduate environmental engineering students. In addition, she was invited at the Korea Institute of Energy Institute and at other leading Korean Universities, where she gave seminars based on the research conducted through this project and more specifically on electrosorption and particle aggregation.

Two of the graduate students who worked on this project, K. Subramaniam and K.-L. Yang, won in 2000 and 2001, respectively, an American Chemical Society (ACS) Graduate Student Award in Environmental Chemistry (awarded to no more than 25 students annually) based on their academic achievements and research. K.-L. Yang and C.J. Chin were awarded a Best Ph.D. Thesis Award from Sigma Xi, The Scientific Research Society, in 2001 and 2002, respectively. K.-L. Yang also won a Molecular Design Institute (MDI) graduate research fellowship based on a submitted research proposal and academic achievements for two consecutive years. This project provided matching funds for the MDI fellowship. The MDI experience gave Yang a unique opportunity to introduce molecular design principles into the environmental engineering field.

The PI of the project has chaired in the past five years the organizing committee for the 77th ACS Colloid and Surface Science Symposium, which was held at GIT during June 15-18, 2003. This Symposium is the premier conference of ACS in the field of colloids and surfaces and highlights the latest scientific advances in this area as well as their applications to other fields, including biotechnology and environmental engineering. More than 500 papers were presented in 10 parallel sessions, and about 500 participants traveled to Atlanta in June and attended the various talks and interacted with other scientists and engineers. Due to the close nature of this project to the theme of the Symposium, the graduate students who worked on the project had the unique opportunity to get involved in the organization of a major conference. Most of them also presented their findings at the Symposium and were able to interact with leading researchers in their research field.

Outreach Activities:

Through this project, the PI had the opportunity to influence and recruit female students to pursue graduate studies in Environmental Engineering. One example is C.C. Tobin, a gifted student in her undergraduate class who was recruited by the PI to conduct research with her and then she was persuaded to attend graduate school. The PI was also able to recruit four female graduate students (K. Subramaniam, C.J. Chin, V. Vithayaveroj, and P. Taboada Serrano) in her research group, representing 50% of the total number of Ph.D. students who have worked with her so far.

Journal Publications

Subramaniam, K., Yiacoumi, S., and Tsouris, C., "Sorption of Copper by Inorganic Particles - Equilibrium, Kinetics, and Particle Interactions: Experimental", Colloids and Surfaces A: Physicochemical and Engineering Aspects, p. 133-146, vol. 177, (2000). Published

Chin, C.J., Yiacoumi, S., Tsouris, C., Relle, S., and Grant, S.B., "Secondary Minimum Aggregation of Superparamagnetic Colloidal Particles", Langmuir, p. 3641-3650, vol. 16, (2000). Published

Chin, C.J., Yiacoumi, S., and Tsouris, C., "Probing DLVO Forces Using Interparticle Magnetic Forces: Transition from Secondary-Minimum to Primary-Minimum Aggregation", Langmuir, p. 6065-6071, vol. 17, (2000). Published

Ying, T.-Y., Yiacoumi, S., and Tsouris, C., "High-Gradient Magnetically Seeded Filtration", Chemical Engineering Science, p. 1101-1113, vol. 55, (2000). Published

Dambies, L., Guimon, C., Yiacoumi, S., and Guibal, E., "Characterization of Metal Ion Interactions with Chitosan by X-Ray Photoelectron Spectroscopy", Colloids and Surfaces A: Physicochemical and Engineering Aspects, p. 203-214, vol. 177, (2001). Published

Yang, K.-L., Ying, T.-Y., Yiacoumi, S., Tsouris, C., and Vittoratos, E. S., "Electrosorption of Ions from Aqueous Solutions by Carbon Aerogel: An Electrical Double-Layer Model", Langmuir, p. 1961-1969, vol. 17, (2001). Published

Shin, W.-T., Yiacoumi, S., Tsouris, C., and Dai, S., "A Pulseless Corona Discharge Process for the Oxidation of Organics in Water", Industrial and Engineering Chemistry Research, p. 4408-4414, vol. 39, (2000). Published

Subramaniam, K., Yiacoumi, S., and Tsouris, C., "Effect of Copper and Cadmium Binding on the Flocculation of Ferric Oxide Particles", Separation Science and Technology, p. 1301-1318, vol. 34, (1999). Published

Chin, C. J., Yiacoumi, S., and Tsouris, C., "Shear-Induced Flocculation of Colloidal Particles in Stirred Tanks", Journal of Colloid and Interface Science, p. 532-545, vol. 206, (1998). Published

Subramaniam, K., and Yiacoumi, S., "Modeling Kinetics of Copper Uptake by Inorganic Colloids under High Surface Coverage Conditions", Colloids and Surfaces A: Physicochemical and Engineering Aspects, p. 145-159, vol. 191, (2001). Published

Chin, C.J., Yiacoumi, S., and Tsouris, C., "Influence of Metal Ion Sorption on Colloidal Surface Forces Measured by Atomic Force Microscopy", Environmental Science & Technology, p. 343-348, vol. 36, (2002). Published

Chin, C.J., Yiacoumi, S., and Tsouris, C., "Agglomeration of Magnetic Particles and Breakup of Magnetic Chains in Magnetorheological Fluids", Colloids and Surfaces A: Physicochemical and Engineering Aspects, p. 63-72, vol. 204, (2002). Published

Ying, T.-Y., Yang, K.-L., Yiacoumi, S., and Tsouris, C., "Electrosorption of Ions from Aqueous Solutions by Nanostructured Carbon Aerogel", Journal of Colloid and Interface Science, p. 18-27, vol. 250, (2002). Published

Yang, K.-L., Yiacoumi, S., and Tsouris, C., "Canonical Monte Carlo Simulations of the Fluctuating-Charge Molecular Water between Charged Surfaces", Journal of Chemical Physics, p. 337-345, vol. 117, (2002). Published

Ying, T.-Y., Yiacoumi, S., and Tsouris, C., "An Electrochemical Method for the Formation of Magnetite Particles", Journal of Dispersion Science and Technology, p. 569-576, vol. 23, (2002). Published

Yang, K.-L., Yiacoumi, S., and Tsouris, C., "Monte Carlo Simulations of Electrical Double-Layer Formation in Nanopores", Journal of Chemical Physics, p. 8499-8507, vol. 117, (2002). Published

Yang, K.-L., Yiacoumi, S., and Tsouris, C., "Proton Adsorption and Electrical Double-Layer Formation inside Charged Platinum Nanochannels", Nano Letters, p. 1433-1437, vol. 2, (2002). Published

Yang, K.-L., Yiacoumi, S., and Tsouris, C., "Electrosorption Capacitance of Nanostructured Carbon Aerogel Obtained by Cyclic Voltammetry", Journal of Electroanalytical Chemistry, p. 159-167, vol. 540, (2003). Published

Chen, J., Yoon, J.-T., and Yiacoumi, S., "Effects of Chemical and Physical Properties of Influent on Copper Sorption onto Activated Carbon Fixed-Bed Columns", Carbon, p. 1635-1644, vol. 41, (2003). Published

Vithayaveroj, V., Yiacoumi, S., and Tsouris, S., "Modification of Surface Forces by Metal Ion Adsorption", Journal of Dispersion Science and Technology, p. 517-525, vol. 24, (2003). Published

Benesch, T., Yiacoumi, S., and Tsouris, C., "Brownian Motion in Confinement", Physical Review E, p. 21401:1-5, vol. 68, (2003). Published

Subramaniam, K., Vithayaveroj, V., Yiacoumi, S., and Tsouris, C., "Copper Uptake by Inorganic Colloids Under High Surface Coverage Conditions: Surface Charge and Sorption Equilibrium Modeling", Journal of Colloid and Interface Science, p. , vol. , (2003). Accepted

Benesch, T., Yiacoumi, S., and Tsouris, C., "Interaction of Colloidal Spheres Close to a Charged Plate", Langmuir, p. , vol. , ( ). Submitted

Shin, W.-T., Garanzuay, X., Yiacoumi, S., Tsouris, C., Gu, B., and Mahinthakumar, K., "Soil-Ozone Interactions: Kinetics and Mathematical Simulation", Journal of Contaminant Hydrology, p. , vol. , ( ). Submitted

Chin, C.J., Lu, S.-C., Yiacoumi, S., and Tsouris, C., "Fractal Dimension of Particle Aggregates in Magnetic Fields", Separation Science and Technology, p. , vol. , ( ). Submitted

Books or Other One-time Publications

Yiacoumi, S., and Chen, J., "Modeling of Metal Ion Sorption Phenomena in Environmental Systems", (1999). Book Chapter, Published
Editor(s): A. Dabrowski
Collection: Adsorption and Its Application in Industry and Environmental Protection
Bibliography: pp. 285-318, Elsevier, Amsterdam

Subramaniam, K., Yiacoumi, S., and Tsouris, C., "A Unified Model for Ion Sorption Kinetics and Colloidal Particle Flocculation Rates", (1998). Conference Proceedings, Published
Editor(s): F. Munier
Collection: Fundamentals of Adsorption 6
Bibliography: pp. 951-956, Elsevier, Paris

Yang, K.-L., Yiacoumi, S., and Tsouris, C., "Electrical Double-Layer Formation at the Nanoscale", (2004). Book Chapter, Accepted
Editor(s): J. A. Schwarz, C. Contescu, and K. Putyera
Collection: Encyclopedia of Nanoscience and Nanotechnology
Bibliography: Marcel Dekker, New York

Vithayaveroj, V., Yiacoumi, S., and Tsouris, C., "Atomic Force Microscopy Studies of
Metal Ion Sorption", (2004). Book Chapter, Accepted
Editor(s): J. A. Schwarz, C. Contescu, and K. Putyera
Collection: Encyclopedia of Nanoscience and Nanotechnology
Bibliography: Marcel Dekker, New York

J.P. Chen, "Metal Ions from Aqueous Solutions: Equilibrium, Kinetics, and Transport", (1997). Thesis, Published
Bibliography: Georgia Institute of Technology, Atlanta, GA

W.-T. Shin, "Effects of Electric Fields on Fluids: Applications in Ozonation", (2000). Thesis, Published
Bibliography: Gorgia Institute of Technology, Atlanta, GA

K. Subramaniam, "Metal Uptake and Its Effects on Colloidal Particle Interactions: Equilibria and Rates", (2000). Thesis, Published
Bibliography: Georgia Institute of Technology, Atlanta, GA

C.J. Chin, "Aggregation of Colloidal Particles and Breakup of Aggregates: Probing Interparticle Forces", (2001). Thesis, Published
Bibliography: Georgia Institute of Technology, Atlanta, GA

T.-Y. Ying, "Environmental Processes Using Electric and Magnetic Fields", (2001). Thesis, Published
Bibliography: Georgia Institute of Technology, Atlanta, GA

K.-L. Yang, "Electrical Double-Layer Formation at the Nanoscale: Molecular Modeling and Applications", (2002). Thesis, Published
Bibliography: Georgia Institute of Technology, Atlanta, GA

V. Vithayaveroj, "Atomic Force Microscopy for Sorption Studies", (2004). Thesis, To Appear
Bibliography: Georgia Institute of Technology, Atlanta, GA

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Contributions

Contributions within Discipline:

The findings of this research provide a better understanding of various fundamental phenomena: (i) influence of sorption of ionic pollutants on particle interactions; (ii) mechanisms of aggregation and breakup of colloidal particles; (iii) interaction mechanisms of metal ions and natural biopolymers; and (iv) interaction mechanisms of ionic species and porous materials. These findings are significant in both engineered and natural environmental systems. They can be used in the design of processes for removing ionic and particulate pollutants from aqueous solutions and in quantifying transport and distribution of pollutants in natural environments.

This research also provides knowledge in using electromagnetic fields to intensify environmental processes. Magnetic fields are used to enhance the removal of particulate pollutants, and electric fields are used to enhance the removal of both inorganic and organic dissolved pollutants. These findings are significant in the design of novel environmental processes.

Contributions to Other Disciplines:

The fundamental aspects of this research have significance in several other disciplines. The knowledge obtained on the aggregation of magnetic colloidal particles and breakup of aggregates has significance in hydrometallurgy to recover mineral ultrafines from aqueous solutions and in magnetorheological fluids for various applications, including vibration controllers. The knowledge from using atomic force microscopy to measure colloidal particle interactions has significance in the characterization and understanding of nanoparticles. The model developed for the sorption of ionic species by porous materials under the influence of an electric field can provide insight into the design of better materials for use in such applications.

The knowledge on the electrical double layer (EDL) formation at the molecular level is important to many interfacial phenomena occurring in physical, chemical, and biological systems. More specifically, the ion transport through the charged channels of biological membranes is controlled by the EDL and the transport rate is determined by the electrical potential distribution and the thickness of EDL inside the channels.

Contributions to Human Resource Development:

Courses were developed and offered to students in Environmental Engineering at GIT. A unique feature of these courses is emphasis on mathematical modeling in environmental systems. Results from the research component of the project were incorporated into the lectures. Students working on the project presented and discussed their research results in front of the class. Courses were offered through the Distance Learning Program of GIT and, therefore, reached industrial researchers and practitioners. In addition, research experience was provided to the students working on the project through visiting appointments at a National Laboratory.

Four female students have participated in the project. One of them (C.C. Tobin) was an undergraduate student who used her research experience through the project to apply and receive a fellowship from NSF; after her research experience, she attended graduate school at Stanford University. Another student (K. Subramaniam) received her Ph.D. degree in 2000 and now she is a project environmental engineer with Environ. A third student, C.J. Chin, completed her Ph.D. in 2001 and has followed an academic career in engineering in Taiwan. V. Vithayaveroj is currently a Ph.D. student in environmental engineering and expects to complete her degree requirements in 2004. Four other students (J.P. Chen, W.-T. Shin, T.-Y. Ying, K.-L. Yang) have completed their Ph.D. degrees through this project and have started reseach or academic careers in engineering. In addition, two students (Y. Sung, T. Benesch) have completed their M.S. degrees by conducting research related to this project, and one of them is working in industry while the other is pursuing a Ph.D. in Environmental Engineering.

Contributions to Resources for Research and Education:

Contributions Beyond Science and Engineering:

Categories for which nothing is reported:

Any Web/Internet Site

Any Product

Contributions: To Any Resources for Research and Education

Contributions: To Any Beyond Science and Engineering